Nitrogen Doping of Graphene Using Electron Beam Generated Plasmas

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ABSTRACT

Graphene, a monolayer of sp^2-hybridized carbon atoms, has attracted much interest for its many potential technological and scientific applications. Of particular interest for sensing applications is that, by varying the surface chemistry of graphene one can control both its electrical properties and its interaction with adsorbates. We have developed a precise and flexible means for functionalizing graphene using electron beam generated plasmas which are characterized by low electron temperatures (< 1 eV) and low incident ion energies (< 5 eV) [1-2]. In this work, we discuss plasma treatments to controllably introduce nitrogen. The chemical, electrical and structural characterization of the functionalized graphene is discussed.

INTRODUCTION

Graphene is viewed as the material of choice in a wide variety of applications because of its unique chemical, physical, and electronic properties. Indeed, the development of graphene-based sensors, circuitry and electronics are areas of intense research. Their development depends strongly on the ability to integrate graphene with other materials and this requires many fundamental advances in the modification of graphene. In particular, the ability to precisely dope graphene and understand the resulting changes in properties will improve integration and broaden the potential application space. Since graphene is essentially two-dimensional, it is very sensitive to the presence of non-carbon species, either on the surface or within the plane. This will change the properties of graphene and can thus be used to alter its reactivity and/or electronic characteristics. In a recent work [1], we have demonstrated the effect of the functionalization of graphene with oxygen and fluorine on the chemical and structural properties of the material using a unique plasma tool developed by the Naval Research Laboratory. In this work the incorporation of nitrogen in graphene is achieved using nitrogen containing gas. Plasmas produced in Ar/N_2 gas mixtures delivers ions and radicals that promote the incorporation of nitrogen.

EXPERIMENTAL

The experimental apparatus has been described in detail elsewhere [2, 3]. Briefly, a magnetically confined electron beam sheet is produced by applying a 2 kV pulse to a linear hollow cathode. The electron beam passed through a slot in a grounded anode and terminated at a second grounded anode. The electron beam sheet results in the ionization volume between the two anodes. The processing stage was located at 2.5 cm from the electron beam axis. The base pressure ($\sim 10^{-6}$ Torr) in the chamber is maintained by a turbo molecular pump. Different gases (Ar, N_2) were introduced through mass flow controllers and the desired operating pressures were achieved by throttling the turbo pump with a conductance limiter. The species flux is monitored by changing the operating pressure from 25 to 90 mTorr of Ar diluted with N_2, where the reactive gas was 5 % of the total flow rate. The plasma was operated at a duty factor of 10 % (2 ms pulse width and 20 ms period) and the total treatment time was 60 seconds (plasma exposure time was 6 sec.). The only changing parameter in this work is the operating pressure which allows the control of the species flux delivered to the surface [4, 5] and thus the doping concentration.

Graphene was produced by CVD growth on copper as described in [6]. The graphene was transferred to a Si/SiO_2 substrate prior to functionalization. The sample was then placed in the vacuum chamber for plasma treatment. After treatment, the functionalized graphene was characterized using ex-situ surface diagnostics. The chemical composition of the samples was identified by XPS (K-Alpha, Thermo scientific). The structure of the samples was examined by Raman spectroscopy (Renishaw). Contact angle measurements (AST VCA goniometer) are used to determine the water wetting contact angle. The electrical properties are verified using two points probe measurement.

RESULTS AND DISCUSSION

Since graphene is a monolayer of carbon, any changes on or within the graphitic surface should be observed by a change in the structural properties through Raman spectroscopy. After plasma treatment in Ar/N_2 at an increasing operating pressure, the Raman spectra shows an increasing defect density as the operating pressure was increased. Figure 1 shows the Raman spectra of graphene and that treated in nitrogen plasma at 90 mtorr. It revealed the increase in the D and D' peaks, signature of disordered carbon atoms, and the decrease of the G and 2D peaks, signature of well ordered sp^2-carbon atoms, intensity. This change in structure is evidently induced by

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the presence of new species on the graphitic plane. The XPS data shows an increase in the nitrogen concentration as well as a broadening in the C1s high resolution XPS data. Figure 2 shows the C1s high resolution XPS spectra of untreated graphene and graphene treated at the highest operating pressure and having the highest dopant level.

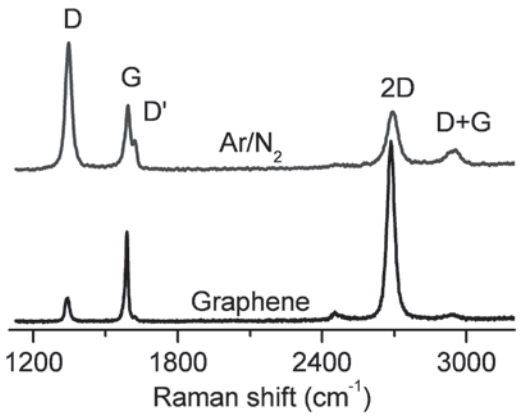

Figure 1: Raman spectra for graphene processed in Ar/N_2 at 90 mTorr pressure.

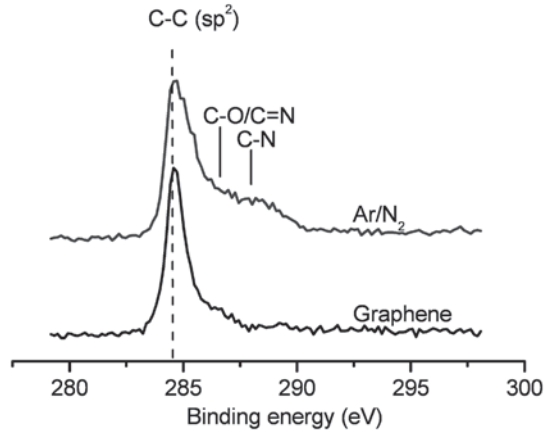

Figure 2: High resolution C1s XPS Spectra for graphene processed in Ar/N_2 at 90 mTorr.

The change in the chemistry induces changes in the chemical reactivity of the graphene but also in the electrical conductivity as shown in Figure 3. The water wetting angle illustrates the change of the surface energy as new compounds (i.e. nitrogen) are added to the graphitic plane. As such, the wettability of the surface inceases and is induced by the increase in the polar component of the surface energy while the dispersive component remained constant. On the other hand, the functionalized graphene at the highest nitrogen concentration remained reasonably conductive compared to those functionalized with oxygen and fluorine at comparable dopant concentrations from references [7, 8, 9] shown in Figure 4. Thus, the functionalized graphene with nitrogen seems to be a better choice to maintain graphene's conductivity than other species, like oxygen or fluorine where their high electronegativity contributes to its drastic decrease [7, 8, 9]. This clearly shows the advantage of using nitrogen for functionalizing graphene in applications where conductivity is a major concern like sensing devices.

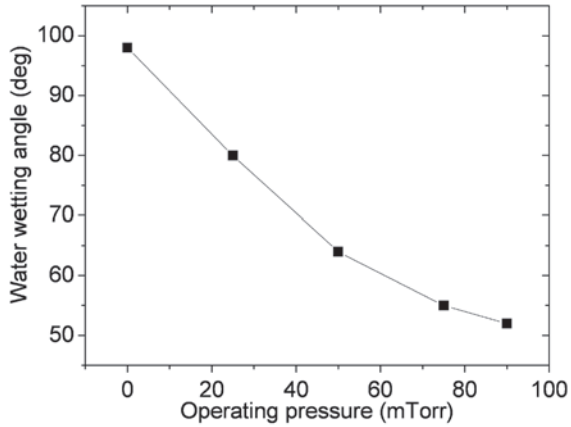

Figure 3: Water contact angle of graphene processed in Ar/N_2, at various operating pressure.

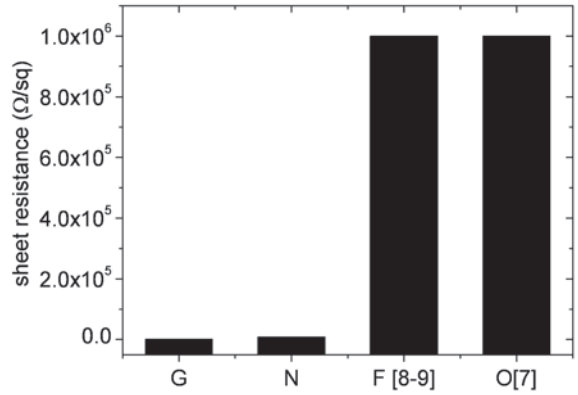

Figure 4: sheet resistance of graphene (G) and graphene treated in nitrogen plasmas at 90 mTorr (N) and those functionalized with oxygen (O)-adapted from ref [7], and fluorine (F)-adapted from refs [8, 9].

CONCLUSION

In summary, nitrogen doping of graphene are achieved using electron beam generated plasmas produced in Ar/N_2 gas mixtures. Nitrogen grafting is verified by XPS and induced the generation of structural defects. Importantly, the nitrogen-doped graphene remained conductive even at the highest dopant levels. This will enable the use of graphene as a platform for sensing devices.

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